

Communications

A New Method for Generating Sn–H Bonds: Reactions of Tin Amides with Silicon Hydrides

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The development of organotin reagents for organic synthesis has been the subject of intense investigation in recent years,¹ with reactions of Bu_3SnH receiving particular attention.² Unfortunately, most of the methods that have been reported require stoichiometric quantities of Bu_3SnH , a significant drawback in light of the toxicity³ and purification⁴ issues that surround triorganotin compounds. To ameliorate these problems while still taking advantage of the unique chemistry of Bu_3SnH , we and others have pursued the design of processes that are catalyzed by Bu_3SnH ; in these reactions, Bu_3SnH effects the key bond-forming step(s), and then a second, innocuous stoichiometric reductant regenerates Bu_3SnH from the initial adduct. To date, two general approaches have been developed, one that relies upon the capacity of borohydrides to reduce Bu_3SnX ($\text{X} = \text{halide}$) to Bu_3SnH ^{5,6} and one that exploits the ability of silicon hydrides to reduce Bu_3SnOR to Bu_3SnH (e.g., see Figure 1).^{7,8}

We are pursuing the extension of this strategy to a third family of reactions of Bu_3SnH , those that generate Bu_3SnNR_2 as intermediates. An obligatory first step in this program is the discovery of an appropriate reductant for the conversion of a Sn–N bond to a Sn–H bond. To the best of our knowledge, only two metal hydrides, B_2H_6 and $n\text{-Bu}_2\text{AlH}$, have been reported to effect this transformation.⁹ However, neither of these species is suitable

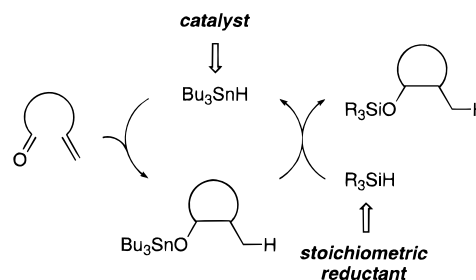
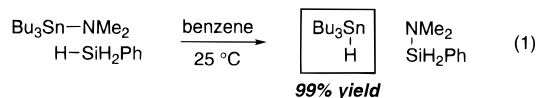


Figure 1. Example of a Bu_3SnH -catalyzed reaction: reductive cyclization of an enal.

as a stoichiometric reducing agent for a Bu_3SnH -catalyzed process, since each is itself reactive toward a wide range of functional groups.

The use of a silicon hydride to reduce Bu_3SnNR_2 to Bu_3SnH is an attractive prospect, since most silicon hydrides are nontoxic and relatively unreactive toward organic functionality.¹⁰ Unfortunately, it has been reported that $\text{Me}_3\text{SnNMe}_2$ does not react with silanes such as Et_3SiH ¹¹ or Ph_3SiH ,¹² even at elevated temperature. Despite these discouraging initial observations, we chose to pursue the discovery of a silicon hydride that can cleanly reduce Bu_3SnNR_2 to Bu_3SnH , and in this communication we describe the successful realization of this objective (eq 1).



Consistent with earlier reports,^{11,12} we found that Et_3SiH and Ph_3SiH do not react with $\text{Bu}_3\text{SnNMe}_2$, even at 80°C (Table 1, entries 1 and 2). In marked contrast, OctSiH_3 , Ph_2SiH_2 , and PhSiH_3 convert $\text{Bu}_3\text{SnNMe}_2$ to Bu_3SnH at room temperature, with varying degrees of effectiveness (entries 3–5); in the case of PhSiH_3 , the reduction is quite efficient (83% yield, entry 5).

The other tin-containing product of these processes (Table 1, entries 3–5) is $\text{Bu}_3\text{SnSnBu}_3$, which is formed from the reaction of Bu_3SnH with $\text{Bu}_3\text{SnNMe}_2$ (eq 2, Sn–Sn bond formation).^{13–15} Thus, efficient generation of Bu_3SnH from $\text{Bu}_3\text{SnNMe}_2$ requires not simply that Sn–H bond formation be chemically competent, but also that it proceed much more rapidly than Sn–Sn bond formation (eq 2). The relative rates of these two pathways can be controlled through choice of reducing agent (Table 1, entries 3–5) and stoichiometry (entries 5 and 6).^{16,17}

Mechanistic studies of the reduction of tin alkoxides by silicon hydrides are consistent with reaction via a four-centered transition state (eq 3, $\text{X} = \text{OR}$), with reduction

(10) For example, see: (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: Boston, 1981. (b) Fleck, T. J. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; pp 4028–4029.

(11) Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295–307.

(12) Neumann, W. P.; Schneider, B.; Sommer, R. *Liebigs Ann. Chem.* **1966**, *692*, 1–11.

(13) Sommer, R.; Neumann, W. P.; Schneider, B. *Tetrahedron Lett.* **1964**, 3875–3878.

(14) After our work was completed, we discovered that Creemers has reported that treatment of $\text{Et}_3\text{SnNMe}_2$ with Ph_2SiH_2 or PhSiH_3 affords $\text{Et}_3\text{SnSnEt}_3$. Et_3SnH is proposed to be an intermediate in this reaction, although it was not observed. Creemers, H. M. J. C. Ph.D. Dissertation, University of Utrecht, 1967.

(1) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: Boston, 1987.

(2) For reviews of the chemistry of Bu_3SnH , see: (a) RajanBabu, T. V. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995. (b) Neumann, W. P. *Synthesis* **1987**, 665–683.

(3) Boyer, I. J. *Toxicology* **1989**, *55*, 253–298.

(4) (a) For a succinct discussion, see: Crich, D.; Sun, S. *J. Org. Chem.* **1996**, *61*, 7200–7201. (b) For polymer-supported R_3SnH , see: Schumann, H.; Pachaly, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1043–1044. (c) For water-soluble R_3SnH , see: Light, J.; Breslow, R. *Tetrahedron Lett.* **1990**, *21*, 2957–2958. Rai, R.; Collum, D. B. *Tetrahedron Lett.* **1994**, *35*, 6221–6224. (d) For fluorinated R_3SnH , see: Curran, D. P.; Hadida, S. *J. Am. Chem. Soc.* **1996**, *118*, 2531–2532.

(5) For the reduction of Bu_3SnX ($\text{X} = \text{halide}$) to Bu_3SnH with borohydrides, see: Birnbaum, E. R.; Javora, P. H. *J. Organomet. Chem.* **1967**, *9*, 379–392.

(6) For catalytic processes, see: (a) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1975**, *40*, 2554–2555. (b) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 303–304.

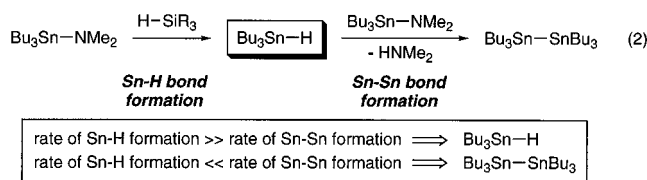
(7) For the reduction of Bu_3SnOR to Bu_3SnH with silicon hydrides, see: (a) Itoi, K. Fr. Patent 1,368,522, 1964. Itoi, K.; Kumano, S. *Kogyo Kagaku Zasshi* **1967**, *70*, 82–86. (b) Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81–94. (c) Bellegarde, B.; Pereyre, M.; Valade, J. *Bull. Soc. Chim. Fr.* **1967**, 3082–3083.

(8) For catalytic processes, see: (a) Nitzsche, S.; Wick, M. *Angew. Chem.* **1957**, *69*, 96. (b) Lipowitz, J.; Bowman, S. A. *Aldrichimica Acta* **1973**, *6*, 1–6. (c) Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 4–5. (d) Hays, D. S.; Scholl, M.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 6751–6752. (e) Lopez, R. M.; Hays, D. S.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 6949–6950.

(9) Kula, M.-R.; Lorberth, J.; Amberger, E. *Chem. Ber.* **1964**, *97*, 2087–2089; *Chem. Abstr.* **1964**, *61*, 7035g.

Table 1. Reaction of Bu₃SnNMe₂ with Silicon Hydrides (1.0 equiv) in Benzene

entry	silane	temp (°C)	t _{1/2} (min)	yield of Bu ₃ SnH (%)
1	Et ₃ SiH	80	no reaction after 28 hours	0
2	Ph ₃ SiH	80	no reaction after 28 hours	0
3	OctSiH ₃	25	17	21
4	Ph ₂ SiH ₂	25	2.5	58
5	PhSiH ₃	25	~ 1	83
6	PhSiH ₃ (5.0 equiv)	25	< 1	99



proceeding more rapidly with alkoxy groups that are less bulky and more basic.^{7,18} We have established that analogous patterns hold for reductions of tin amides by silicon hydrides. Thus, less hindered Bu₃SnNMe₂ reacts much more rapidly with PhSiH₃ than does Bu₃SnN(*i*-Pr)₂

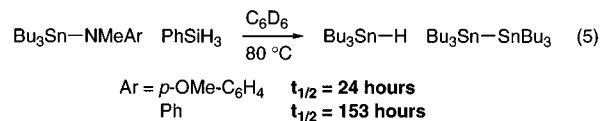
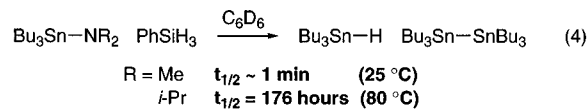
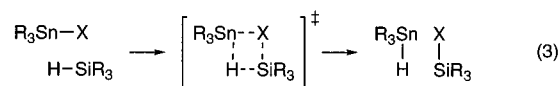
(15) In the reaction of Bu₃SnNMe₂ with PMHS (polymethylhydrosiloxane; TMSO-(SiHMeO)_{*n*}-TMS) or Et₂SiH₂, Bu₃SnSnBu₃ is the major (>90%) tin-containing product.

(16) Treatment of Bu₃SnNMe₂ with 5.0 equiv of Ph₂SiH₂ affords Bu₃SnH in 88% yield.

(17) The ratio of silicon hydride to Bu₃SnNR₂ will be large for Bu₃SnH-catalyzed processes (stoichiometric silicon hydride, catalytic tin), thereby favoring formation of Bu₃SnH at the expense of Bu₃SnSnBu₃.

(18) Pijsselman, J.; Pereyre, M. *J. Organomet. Chem.* **1973**, *63*, 139–157.

(eq 4), and more electron-rich Bu₃SnNMe(*p*-OMe-C₆H₄) reacts more quickly than Bu₃SnNMePh (eq 5).



In conclusion, we have discovered a new Sn-H bond-forming reaction, the reduction of a Sn-N bond by a silicon hydride, and we have developed conditions that produce the tin hydride in quantitative yield. Furthermore, we have determined the impact of steric and electronic effects on the rate of reduction of the Sn-N bond. We are currently exploring applications of this new reaction in Bu₃SnH-catalyzed processes.

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Supporting Information Available: Experimental procedures and compound characterization data (21 pages).

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